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TECHNICAL NOTE

STRUCTURAL STUDIES OF LINEAR MOLECULES BY.
MICROWAVE SPECTROSCOPY

J. K. Tyler and J. Sheridan

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STRUCTURAL STUDIES OF LINEAR MOLECULES BY
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Abstract

Rotational constants have been measured for three isotopic forms
of fluorine cyanide, six isotopic forms of fluoroacetylene, and for the
species $^{35}ClC^{15}N$, $^{37}ClC^{15}N$, $IC^{15}N$, $^{35}Cl^{13}CCH$ and $^{35}ClC^{13}CH$.
Accurate bond-distances have been computed for all the halogen cyanides
and for fluoro- and chloroacetylene, by the method of isotopic substitution
at all atoms (except F and I). The CF bonds in these compounds are
the shortest yet found. The CN distance is virtually constant at 1.159 A.
The nuclear quadrupole coupling constant for nitrogen-14 in fluorine
cyanide, -2.67 Mc/s, is the lowest yet measured for a cyanide grouping.
The dipole moments of fluorine cyanide and fluoroacetylene, from Stark
effects, are 2.17 D and 0.75 D respectively. Rotation spectra of molecules
in excited bending vibrational states are analysed for fluorine cyanide,
fluoroacetylene and cyanoacetylene ~~abstract~~

The present work is part of a series of studies of internuclear
distances and electronic structures of simple molecules from their
rotation spectra. Although there has been considerable microwave work
on linear molecules, the data have been insufficient for the derivation
of the most complete structural information in certain simple systems.
Moreover, fluorine cyanide and fluoroacetylene, the first substances
to contain fluorine attached to a triply bonded carbon atom, have only
recently been prepared. Studies of these two substances are described
in detail here, following brief preliminary communications[1,2]. Data for
rare isotopic forms of related linear molecules have also been measured
when necessary for the present treatment.

Costain[3] has emphasized that when, as nearly always at present,
insufficient equilibrium moments of inertia are available for derivation
of equilibrium parameters, the best estimates of internuclear distances

are made from the changes in the ground-state moments of inertia caused by
isotopic substitution at each atom. We have now obtained enough data to
apply these methods in the fullest possible way to fluorine cyanide, chlorine
cyanide and iodine cyanide, and also chloro- and fluoroacetylene. Special
considerations arising from the lack of a second isotope of fluorine, and
occasionally from 'he smallness of certain isotopic shifts, have been made
in ways indicated in earlier treatments[3,4].

In addition, we have measured the electric dipole moments of fluorine
cyanide and fluoroacetylene from the Stark effects in their spectra, and
the nuclear quadrupole coupling constant of nitrogen-14 in fluorine cyanide.
Rotation spectra of these two molecules, and of cyanoacetylene, in
excited levels of degenerate vibrational modes, have also been analysed.

We believe that the results of these measurements allow as accurate
a comparison as is possible at present between the structures of these
molecules.

EXPERIMENTAL

MATERIALS

Initial work on fluorine cyanide was carried out with impure samples
in which this substance was first detected by infra-red spectroscopy[5].
Fawcett and Lipscomb[6] have described the preparation of pure fluorine
cyanide by the pyrolysis of cyanuric trifluoride at 1200°C in a carbon
tube packed with carbon chips. We have found that fluorine cyanide
is produced in good yield by passing the vapour of cyanuric trifluoride
over a white hot platinum spiral, followed by vacuum fractionations
monitored by infra-red spectra. The samples used were sufficiently
pure for ready observation of the spectra of $F^{13}CN$ and $FC^{15}N$ in their
natural abundances.

The preparation of fluoroacetylene followed that of Middleton and
Sharkey[7]. Deutero-fluoroacetylene was obtained by direct exchange
with alkaline deuterium oxide. Infra-red analysis of both samples showed
that they were virtually pure.

Chlorine cyanide[8], iodine cyanide[9], and chloroacetylene[10] were prepared by standard methods. Cyanoacetylene was obtained by the dehydration of propiolic amide with phosphorus pentoxide[11], and a portion deuterated by exchange with deuterium oxide.

SPECTROSCOPIC METHODS

Absorption frequencies were measured in a spectrometer employing Stark effect modulation at 100 kc/s, of essentially conventional design to be briefly described elsewhere[12]. For highest resolution of stronger absorptions, and for work above 45,000 Mc/s, a simple video spectrometer[13] was used. The absorption cells were cooled to -78°C for all studies except those of iodine cyanide. The spectra of all the species containing carbon-13 or nitrogen-15 were measured at the natural concentrations of these isotopes. Stark effect displacements were measured in the usual way by addition of a d.c. potential to the modulation, the electric field in the cell being calibrated from Stark displacements measured under the same conditions for the $J = 1 \to 2$ transition of carbon oxysulphide, for which the dipole moment was taken as 0.7124D.

RESULTS

Measured frequencies, with thier assignments, are listed in table 1.

TABLE 1. MEASURED FREQUENCIES (Mc/s)

Fluorine Cyanide

Transition		Transition	
$F^{12}C^{14}N$		$J 2 \to 3$ $v = 0$	
$J 0 \to 1$ $v = 0$			
$F1 \to 1$	21107.71	$F1 \to 2$	
$F1 \to 2$	21108.50	$F2 \to 3$	63324.60
$F1 \to 0$	21109.69	$F3 \to 4$	
$J 1 \to 2$ $v = 0$			
$F2 \to 2$		$v = 1, \ell = \pm 1$	63447.99
$F0 \to 1$	42215.86	(ν_2)	63567.06
$F1 \to 2$			
$F2 \to 3$	42216.64	$F^{13}C^{14}N$	
$F2 \to 1$	-	$J 0 \to 1$ $v = 0$	
$F1 \to 1$	42217.94	$F1 \to 2$	21095.71
		$F^{12}C^{15}N$	
		$J 0 \to 1$ $v = 0$	20372.32

Chlorine Cyanide

Transition	$^{35}Cl^{12}C^{14}N$	$^{35}Cl^{12}C^{15}N$	$^{37}Cl^{12}C^{14}N$	$^{37}Cl^{12}C^{15}N$
J2→3				
F½→3/2, 3/2→5/2	35820.93	34484.32	35080.32	33755.32
F5/2→7/2, 7/2→9/2	35825.77	34489.21	35084.14	33759.18

Iodine Cyanide

Transition	$^{127}I^{12}C^{14}N$	$^{127}I^{12}C^{15}N$
J4→5		
F9/2→11/2	32243.41	30819.59
F13/2→15/2	32268.32	30839.63
F11/2→13/2	32278.36	30849.90

Fluoroacetylene

Transition	FCCH	FCCD
J 0→1 v = 0	19412.37	17472.08
J 1→2 v = 0	38824.64	34944.07
v = 1, $\ell = \pm 1$ (ν_5)	38834.69	34978.02
	38884.96	35031.04
v = 1, $\ell = \pm 1$ (ν_4)	38896.94	35011.51
	38973.41	35072.82
J3→4 v = 0	77648.58	69887.66

Transition	$F^{13}CCH$	$F^{13}CCD$
J 0→1 v = 0	19401.12	17467.82
J 1→2 v = 0	38802.53	34935.56

Transition	$FC^{13}CH$	$FC^{13}CD$
J 0→1 v = 0	19747.94	—
J 1→2 v = 0	37495.67	33944.93

Chloroacetylene

Transition	$^{35}ClCCH$	$^{35}Cl C^{13} CH$	$^{35}Cl^{13}CCH$
J 2→3			
F 7/2→9/2, 5/2→7/2	34106.09	32819.35	33934.10

Cyanoacetylene

Transition		Transition	
HCCCN		$v = 1$, $\ell = {}^+_- 1$	
		(ν_7)(cont)	
J $0 \to 1$ $v = 0$		F $2 \to 2$	
F $1 \to 1$	9097.09		
F $1 \to 2$	9098.36		
F $1 \to 0$	9100.32	F $3 \to 3$	27399.69
	9145.92	F $2 \to 3$	27400.37
$v = 2$, $\ell = 0$ $\{$ 9154.88		F $1 \to 2$ $\}$	27400.74
(ν_7) $\{$ 9156.09		F $3 \to 4$ $\}$	
J $2 \to 3$ $v = 0$		F $2 \to 2$	—
F $3 \to 3$	27292.94		27436.63
F $1 \to 2$	27294.06	$v = 2$ $\ell = 0, {}^+_- 2$	27466.42
F $2 \to 3$ $\}$ 27294.33		(ν_7)	27467.73
F $3 \to 4$ $\}$		**J $3 \to 4$ $v = 0$**	
F $2 \to 2$	27296.20	F $4 \to 4$	36390.89
$v = 1$, $\ell = {}^+_- 1$ $\{$ 27297.18		F $4 \to 5$	
(ν_5) $\{$ 27312.47		F $3 \to 4$ $\}$ 36392.36	
$v = 1$, $\ell = {}^+_- 1$ $\{$ 27339.13		F $2 \to 3$ $\}$	
(ν_6) $\{$ 27360.47		F $3 \to 3$	36394.18
$v = 1$, $\ell = {}^+_- 1$		$v = 1$, $\ell = {}^+_- 1$ $\{$ 36395.91	
(ν_7)		(ν_5) $\{$ 36416.51	
F $3 \to 3$	27360.47	$v = 1$, $\ell = {}^+_- 1$ $\{$ 36452.08	
F $2 \to 3$	27361.12	(ν_6) $\{$ 36480.68	
F $1 \to 2$ $\}$ 27361.51			
F $3 \to 4$ $\}$			

$$J = 3 \to 4 \text{ (Contd.)}$$

Transition		Transition	
$v = 1$, $\ell = {}^+_- 1$		**J $7 \to 8$ $v = 0$**	72783.79
(ν_7)		$v = 1$, $\ell = {}^+_- 1$ $\{$ 72790.50	
F $4 \to 4$		(ν_5) $\{$ 72831.45	
F $3 \to 4$	36481.72	$v = 1$, $\ell = {}^+_- 1$ $\{$ 72902.44	
F $4 \to 5$ $\}$ 36481.88		(ν_6) $\{$ 72960.43	
F $2 \to 3$ $\}$		$v = 1$, $\ell = {}^+_- 1$	72962.63
F $3 \to 3$	36483.28	(ν_7)	73067.27

Cyanoacetylene (Continued)

$\frac{I = 3 \to 4, \ (Contd.)}{v=1 \ \ell = -1 \ (\nu_7)}$		J $9 \to 10$ v = 0	90979.05
F $4 \to 4$	36532.94	v = 1, $\ell = \pm 1$	$\{$ 90987.30
F $3 \to 4$	36534.04	(ν_5)	91038.60
F $4 \to 5$ $\}$	36534.17	v = 1, $\ell = \pm 1$	$\{$ 91128.49
F $2 \to 3$ $\}$		(ν_6)	91200.03
F $3 \to 3$	36535.54	v = 1, $\ell = \pm 1$	$\{$ 91202.64
	36582.17	(ν_7)	91332.15
	36583.69	DCCCN	
v = 2, $\ell = 0, \pm 2$ $\{$	36622.25	J $3 \to 4$ v = 0	33772.56
(ν_7)	36623.51	v = 1, $\ell = \pm 1$	$\{$ 33796.08
		(ν_5)	33817.54
v = 3, $\ell = \pm 1$ $\{$	36684.90	v = 1, $\ell = \pm 1$	33822.62
(ν_7)	36789.99	(ν_6)	33847.40
v = 3, $\ell = \pm 3$ $\{$	36737.14	v = 1, $\ell = \pm 1$	33852.65
(ν_7)	36738.32	(ν_7)	33898.97
		v = 2, $\ell = 0, \pm 2$	33979.29
		(ν_7)	

The estimated experimental uncertainties are $\pm$ 0.1 Mc/s, except for lines of rare isotopic species, where the errors may reach twice this. Table 2 gives the derived rotational constants for the ground states, while the centrifugal distortion constants, D_J, are listed in Table 3, with values of the constants α, representing the effects of various vibrational quanta on the rotational constant B, and the corresponding ℓ-type doubling constants, q. For the assignments given, the line-frequencies calculated from these constants agree with observation within the error of measurement in virtually all cases. Relative intensities were in agreement with the assignments.

Stark effect displacements are summarised in table 4 for the J = $0 \to 1$ transition of FCN and the J = $0 \to 1$ and $1 \to 2$ transitions of FCCH. The effect of the small nuclear quadrupole splitting in FCN was neglected in comparison with the large Stark displacements.

TABLE 2

GROUND STATE ROTATIONAL CONSTANTS, B_0, (Mc/s)

Molecule	B_0 (Mc/s)
FCN	$10,554.20 \pm 0.02$
$F^{13}CN$	$10,547.80 \pm 0.05$
$FC^{15}N$	$10,186.42 \pm 0.05$
$^{35}ClC^{15}N$	$5,748.061 \pm 0.03$
$^{37}ClC^{15}N$	$5,626.425 \pm 0.03$
FCCH	$9,706.19 \pm 0.01$
$F^{13}CCH$	$9,700.65 \pm 0.02$
$FC^{13}CH$	$9,373.94 \pm 0.02$
FCCD	$8,736.04 \pm 0.01$
$F^{13}CCD$	$8,733.92 \pm 0.02$
$FC^{13}CD$	$8,486.26 \pm 0.02$
$IC^{15}N$	$3,032.661 \pm 0.02$
$^{35}Cl^{13}CCH$	$5,655.57 \pm 0.03$
$^{35}ClC^{13}CH$	$5,469.73 \pm 0.03$
HCCCN	$4,549.06 \pm 0.01$
DCCCN	$4,221.58 \pm 0.01$

TABLE 3

ROTATION - VIBRATION CONSTANTS

Molecule		α Mc/s	q Mc/s	D_J Kc/s
FCN	ν_2	-30.39 ± 0.1	19.85 ± 0.1	5.3 ± 0.5
FCCH	ν_4	-27.65 ± 0.05	19.12 ± 0.05	3.6 ± 0.5
	ν_5	-8.82 ± 0.05	12.57 ± 0.05	
FCCD	ν_4	-24.56 ± 0.05	15.33 ± 0.05	2.6 ± 0.5
	ν_5	-15.15 ± 0.05	13.26 ± 0.05	
HCCCN	ν_5	-1.73 ± 0.02	2.56 ± 0.02	0.56 ± 0.01
	ν_6	-9.24 ± 0.02	3.57 ± 0.02	
	ν_7	-14.46 ± 0.02	6.54 ± 0.02	
DCCCN	ν_5	-4.28 ± 0.05	2.63 ± 0.05	
	ν_6	-7.81 ± 0.05	3.10 ± 0.05	
	ν_7	-12.91 ± 0.05	5.79 ± 0.05	

TABLE 4

STARK EFFECT MEASUREMENTS

FCN J $0 \to 1$

$E^2 \times 10^{-4}$ (v/cm)^2	30.90	85.84	123.60
$\Delta \nu$ Mc/s M = 0	9.21	26.34 v	37.54

$$\mu = 2.17 \overset{+}{-} 0.05 \text{ Debye units}$$

FCCH J $1 \to 2$

$E^2 \times 10^{-4}$ (v/cm)^2		50.09	78.27	153.40
$\Delta \nu$ Mc/s	M = 0	-0.48	-0.74	-1.56
	M = 1	0.46	0.68	1.28

$$\mu = 0.73 \overset{+}{-} 0.03 \text{ Debye units}$$

TABLE 5

MOLECULAR PROPERTIES

(All bond lengths in A)

	$\mu(D)$	Nuclear quadrupole coupling constant of nitrogen-14 (Mc/s)
H $\underline{1.063}$ C $\underline{1.155}$ N	3.00	$-4.58 \overset{+}{-} 0.05$
F $\underline{1.262}$ C $\underline{1.159}$ N	2.17	$-2.67 \overset{+}{-} 0.05$
Cl $\underline{1.631}$ C $\underline{1.159}$ N	2.80	$-3.63 \overset{+}{-} 0.1$
Br $\underline{1.789}$ C $\underline{1.158}$ N	2.94	$-3.83 \overset{+}{-} 0.08$
I $\underline{1.994}$ C $\underline{1.159}$ N	3.71	$-3.80 \overset{+}{-} 0.1$
F $\underline{1.279}$ C $\underline{1.198}$ C $\underline{1.053}$ H	0.73	-
Cl $\underline{1.637}$ C $\underline{1.204}$ C $\underline{1.055}$ H	0.44	-
H $\underline{1.058}$ C $\underline{1.205}$ C $\underline{1.378}$ C $\underline{1.159}$ N 3.6		$-4.28 \overset{+}{-} 0.05$

The Stark effects for these linear molecules are of the expected second-order type, and yield values of 2.17 $\overset{+}{-}$ 0.05 D and 0.73 $\overset{+}{-}$ 0.03 D for the electric dipole moments of FCN and FCCH respectively. The disagreement with the value earlier reported[1] for FCN arises from an error in calibration in the preliminary work. No measurements of dipole moment by dielectric methods are available for these substances.

Deutero-fluoroacetylene, FCCD, is an unusual example of a molecule in which deuterium is the only quadrupolar nucleus, and which has its $J = 0 \to 1$ transition in the 1 cm wavelength region. In view of the resolution[14] of deuterium quadrupole splitting in ClCCD an attempt was made to resolve such hyperfine structure in the $J = 0 \to 1$ line of FCCD at low gas-pressures in the video spectrometer. No splitting could be detected at a line-width of 150 kc/s at half intensity, and it was concluded that the deuterium coupling is not markedly greater than in ClCCD, where the splittings would be close to the resolution limit of our instruments.

In table 5 are listed the internuclear distances (r_s) determined by the isotopic substitution method from well known formulae summarized by Kraitchman[15]. With the data now reported, and existing measurements[16], all atoms have now been located in this way, except fluorine and iodine, where isotopic replacement is not normally possible. These atoms have been located from knowledge of the coordinates of all other atoms and of the centre of gravity of the molecule, in the way recommended by Costain[3], making use of the observation that the relation $\sum mx_s = 0$ is obeyed, where x_s is the substituion distance of an atom from the molecular mass centre. Since the truth of this relation is further confirmed here for chlorine cyanide and chloroacetylene, in which all atoms are located by substitution, the belief that F and I atoms are accurately located by this means in the related compounds is strongly supported. Also included in table 5 are the r_s- structure of bromine cyanide, entirely determinable from previous work[16], and the structure of hydrogen cyanide[3], as well as data on dipole moments and quadrupole coupling constants of nitrogen. The r_s- structure of cyanoacetylene[3], determined from the data of Westenberg and Wilson[17], is also included for comparison. Measurements on carbon-13 and nitrogen-15 species of HCCN and DCCN were also made during the present work; agreement with the findings of Westenberg and Wilson was very close, and our measurements give the same r_s- structure. In some instances, r_s- distances in these molecules can be computed independently in more than one way. In all such cases the

agreement between values is very close, within 0.001 A; a mean was taken in rounding the result to the nearest 0.001 A.

The accuracy of the internuclear distances is at present difficult to estimate absolutely. Costain[3] has expressed the view that r_s - distances, obtained from displacements similar to most of those concerned here, should be within 0.002 A of the equilibrium nuclear separations. Although such a view may be sometimes optimistic, we have adopted it for a general basis of discussion of our results, partly because it is a possible degree of accuracy, and one superior to that of other methods of estimating these distances at the present time, and partly because any deficiencies in the r_s - method should be less important when comparisons are made, as here, between series of molecules of closely related geometry. In fluorine cyanide and fluoroacetylene the carbon of the CF bond is within 0.1 - 0.18 A of the molecular mass centre, and the corresponding carbon-13 shifts, although accurately measured and still in the range estimated to be acceptable[3], are small. Hence it is these carbon atoms which, if any, might be somewhat less accurately placed than in the general case. Against this, it must be recorded that, when the location of the carbon of the CF bond is made independently in $HCCF$ and $DCCF$, the r_s - distances are in very close agreement.

For fluoroacetylene, sufficient forms were studied for a check to be made[2] by means of the "double substitution" or "second difference" method described by Pierce[4]. In this, the r_s - coordinate (r_x) of an atom X is obtained for the original molecule, and again ($r_{x'}$) for a species substituted with extra mass Δ m at another atom, Y. The distance (r_y) of Y from the centre of gravity of the original species is then given by ($r_k - r_{k'}$)(M + Δ m)/ Δ m, M being the original molecular mass. If X is well away from the mass centre, $r_k - r_{k'}$ is accurately obtainable, and r_y may be computed. When data for $FCCH$, $FCCD$, $F^{13}CCH$ and $F^{13}CCD$ are used in this way to locate the carbon atom of the CF bond, its r_y is found as 0.1744 A, as against 0.1740 A from the direct isotopic shift. This agreement thus lends support to the distances found in the simpler way. If the "double substitution" coordinate is used for this

atom in conjunction with r_s coordinates for the remainder, fluorine being located as already indicated, the structure becomes $CF = 1.280$ A, $CC = 1.197$ A, $CH = 1.053$ A, hardly differing from that in table 5.

Enough data are available to apply the second difference method to locate all isotopically replaceable atoms in fluoroacetylene. The present data, so applied, give the structure: $CF = 1.234$ A, $CC = 1.203$ A, $CH = 1.058$ A. There is, however, no proven disagreement with the tabulated r_s structure, since it should be emphasized that the second difference method makes exceptional demands on the accuracy of the rotational constants, or at least of their isotopic shifts. This is apparent from the relationship mentioned, through which uncertainties in r_k are multiplied in r_y by the ratio $(M + \ldots m)/\Delta m$, here about 45. Even with the very small uncertainties in B_o values given in table 2 for fluoroacetylene, it still emerges that coordinates of all atoms located by second differences are uncertain by some ± 0.005 A from possible errors in relative B_o values alone. Hence the usual r_s - structure is much to be preferred at present; the improbability of the structure derived above entirely by the double substitution method may be emphasised by noting that it would have a moment of inertia nearly 1% greater than the observed ground state moment. As high frequency studies permit continued refinement of rotational constants for the necessary isotopic forms, closer comparison of structures from the single and the double substitution methods will be possible.

DISCUSSION

The CF distances measured here are the first to be determined for carbon atoms triply bonded to a second ligand; they are easily the shortest CF distances yet found, that in fluoracetylene being some 8% shorter than the 1.38 A found in methyl fluoride[18] and ethyl fluoride[19], while the CF in fluorine cyanide is 9% shorter than the same value. In vinyl fluoride[20] and other substances containing the group $=CHF$[21], the CF length (1.34A - 1.35A) is some 3% less than in alkyl fluorides. These percentage

shortenings are close to those found for CCl bonds in the series: ethyl chloride[22] (1.788A), vinyl chloride[23] (1.726A) and chloracetylene (1.637A) or chlorine cyanide (1.631A). The CCl in chloracetylene is some 0.005A longer than the length previously reported[24] from more restricted microwave data which did not allow r_s-distances to be computed. The new length agrees closely with that in methyl chloracetylene[25], as predicted by Costain[25] on the basis of the equality of the chlorine quadrupole couplings in these two substances.

A discussion of the nature of the carbon-halogen bonds in these substances, based purely on their lengths, can be given in various terms, but is inconclusive regarding the question of how much double-bond character is involved. Shortenings expected on account of reduction of the carbon bond-radius with increasing s-character in carbon bonding orbitals[26] are less than those observed, provided constant halogen radii are assumed. Thus the maximum shortenings due to changes in carbon radius which might reasonably occur are the changes in "single" carbon-carbon bond lengths in propane[27] (1.526A), propene[28] (1.501A) and methyl acetylene[29] (1.453A), and even part of these shortenings can legitimately be regarded[30] as due to hyperconjugation. A more complicated situation is thus very probable for the carbon-halogen bonds in these substances. Explanations which do not necessarily involve double-bond character might ascribe important effects to the presence or absence of interactions between non-bonded atoms[31], or to variations in hybridization of orbitals in accordance with electronegativities of substituents,[32] but quantitative discussion is difficult. On the other hand, a model which allows conjugation effects to confer some double-bond character on the shorter carbon-halogen bonds[23,33,34] permits the simplest explanation of the results, and conforms with a reasonable and widely held view. Pauling[35] has emphasized that such double-bond character would be especially favoured when, as in the present linear molecules, two equivalent pairs of π-orbitals can be used by the atoms concerned. Accordingly we regard the CF bonds in fluorine

cyanide and fluoroacetylene as 'possessing double bond character, although quantitative estimates are prevented by the difficulties in ascribing atomic radii. A tendency of fluorine, as a first-row element, to form double bonds accords with general chemical experience, but in the molecules under discussion the effects for fluorine are no greater than those for chlorine. It is notable, however, that the CF distance in FCN is 0.017A shorter than in fluoroacetylene, while in the analogous chlorine compounds the difference, though in the same direction, is only 0.006A.

The stretching force constant for the CF bond in FCN was determined by Dodd and Little[36], and that for CF in fluoroacetylene by Brown and Tyler[37]. Similar treatments for fluoroacetylene and other halogenated acetylenes were given by Hunt and Wilson[38]. These carbon-halogen force constants are all much higher than in corresponding alkyl halides and are to be correlated with them through concepts similar to those mentioned in discussing the bond-lengths.

The nature of the CX bonding in the XCN series should be reflected in properties of the CN linkage and in the nuclear quadrupole coupling of the nitrogen-14 atom. In FCN this coupling is the smallest yet found for a cyanide group, being only some 58% of than in HCN. The nitrogen couplings decrease as we move along the XCN series in the order $X = H, I, Br, Cl, F$ (Table 5). This is in agreement with the suggestion of Townes and Dailey, and others[39], that states containing $C = N^-$, with low quadrupole coupling, increase in importance in the same X sequence. In early work[40], this sequence was also believed to be accompanied by a small steady increase in CN length, but the present results show that the substitution CN distance is very close to 1.159A in all the halogen cyanides, though this is probably slightly longer than the value in HCN. Thus, while CN lengths suggest that states containing $C = N^-$ are somewhat more important in the halogen cyanides than in HCN, they give no indication of a variation within the halogen cyanides themselves.

are made from the changes in the ground-state moments of inertia caused by isotopic substitution at each atom. We have now obtained enough data to apply these methods in the fullest possible way to fluorine cyanide, chlorine cyanide and iodine cyanide, and also chloro- and fluoroacetylene. Special considerations arising from the lack of a second isotope of fluorine, and occasionally from the smallness of certain isotopic shifts, have been made in ways indicated in earlier treatments[3,4].

In addition, we have measured the electric dipole moments of fluorine cyanide and fluoroacetylene from the Stark effects in their spectra, and the nuclear quadrupole coupling constant of nitrogen-14 in fluorine cyanide. Rotation spectra of these two molecules, and of cyanoacetylene, in excited levels of degenerate vibrational modes, have also been analysed.

We believe that the results of these measurements allow as accurate a comparison as is possible at present between the structures of these molecules.

EXPERIMENTAL

MATERIALS

Initial work on fluorine cyanide was carried out with impure samples in which this substance was first detected by infra-red spectroscopy[5]. Fawcett and Lipscomb[6] have described the preparation of pure fluorine cyanide by the pyrolysis of cyanuric trifluoride at 1200°C in a carbon tube packed with carbon chips. We have found that fluorine cyanide is produced in good yield by passing the vapour of cyanuric trifluoride over a white hot platinum spiral, followed by vacuum fractionations monitored by infra-red spectra. The samples used were sufficiently pure for ready observation of the spectra of $F^{13}CN$ and $FC^{15}N$ in their natural abundances.

The preparation of fluoroacetylene followed that of Middleton and Sharkey[7]. Deutero-fluoroacetylene was obtained by direct exchange with alkaline deuterium oxide. Infra-red analysis of both samples showed that they were virtually pure.

Chlorine cyanide[8], iodine cyanide[9], and chloroacetylene[10] were prepared by standard methods. Cyanoacetylene was obtained by the dehydration of propiolic amide with phosphorus pentoxide[11], and a portion deuterated by exchange with deuterium oxide.

SPECTROSCOPIC METHODS

Absorption frequencies were measured in a spectrometer employing Stark effect modulation at 100 kc/s, of essentially conventional design to be briefly described elsewhere[12]. For highest resolution of stronger absorptions, and for work above 45,000 Mc/s, a simple video spectrometer[13] was used. The absorption cells were cooled to -78°C for all studies except those of iodine cyanide. The spectra of all the species containing carbon-13 or nitrogen-15 were measured at the natural concentrations of these isotopes. Stark effect displacements were measured in the usual way by addition of a d.c. potential to the modulation, the electric field in the cell being calibrated from Stark displacements measured under the same conditions for the $J = 1 \to 2$ transition of carbon oxysulphide, for which the dipole moment was taken as 0.7124D.

RESULTS

Measured frequencies, with thier assignments, are listed in table 1.

TABLE 1. MEASURED FREQUENCIES (Mc/s)

Fluorine Cyanide

Transition		Transition	
$F^{12}C^{14}N$		$J2 \to 3 \quad v = 0$	
$J\ 0 \to 1 \quad v = 0$			
$F1 \to 1$	21107.71	$F1 \to 2$	
$F1 \to 2$	21108.50	$F2 \to 3$	63324.60
$F1 \to 0$	21109.69	$F3 \to 4$	
$J1 \to 2 \quad v = 0$			
$F2 \to 2$		$v = 1, \ell = \pm 1$	63447.99
$F0 \to 1$	42215.86	(γ_2)	63567.06
$F1 \to 2$			
$F2 \to 3$	42216.64	$F^{13}C^{14}N$	
$F2 \to 1$		$J\ 0 \to 1 \quad v = 0$	
$F1 \to 1$	42217.94	$F1 \to 2$	21095.71
		$F^{12}C^{15}N$	
		$J\ 0 \to 1 \quad v = 0$	20372.32

Chlorine Cyanide

Transition	$^{35}Cl^{12}C^{14}N$	$^{35}Cl^{12}C^{15}N$	$^{37}Cl^{12}C^{14}N$	$^{37}Cl^{12}C^{15}N$
J2→3				
F1/2→3/2, 3/2→5/2	35820.93	34484.32	35080.32	33755.32
F5/2→7/2, 7/2→9/2	35825.77	34489.21	35084.14	33759.19

Iodine Cyanide

Transition	$^{127}I^{12}C^{14}N$	$^{127}I^{12}C^{15}N$
J4→5		
F9/2→11/2	32243.41	30819.59
F13/2→15/2	32263.32	30839.63
F11/2→13/2	32278.36	30849.90

Fluoroacetylene

Transition	FCCH	FCCD
J0→1 v = 0	19412.37	17472.08
J1→2 v = 0	38824.64	34944.07
v = 1, $\ell = \pm 1$ (ν_5)	{ 38834.69 / 38884.96 }	{ 34978.02 / 35031.04 }
v = 1, $\ell = \pm 1$ (ν_4)	{ 38896.94 / 38973.41 }	{ 35011.51 / 35072.82 }
J3→4 v = 0	77648.58	69887.66
	$F^{13}CCH$	$F^{13}CCD$
J0→1 v = 0	19401.12	17467.82
J1→2 v = 0	38802.53	34935.56
	$FC^{13}CH$	$FC^{13}CD$
J0→1 v = 0	18747.94	-
J1→2 v = 0	37495.67	33944.93

Chloroacetylene

Transition	$^{35}ClCCH$	$^{35}Cl^{13}CCH$	$^{35}Cl^{13}CCH$
J 2→3			
F 7/2→9/2, 5/2→7/2	34106.09	32819.35	33934.10

Cyanoacetylene

Transition			Transition	
HCCCN			$v = 1, \ell = {}^+_- 1$	
J 0→1 v = 0			(ν_7)(cont)	
F 1→1	9097.09		F 2→2	
F 1→2	9098.36			
F 1→0	9100.32		F 3→3	27399.69
	9145.32		F 2→3	27400.37
$v = 2, \ell = 0$	9154.88		F 1→2	27400.74
(ν_7)	9156.09		F 3→4	
J 2→3 v = 0			F 2→2	-
F 3→3	27292.94			27436.63
F 1→2	27294.06		$v = 2\, \ell = 0, {}^+_- 2$	27466.42
F 2→3	27294.33		(ν_7)	27467.73
F 3→4				
F 2→2	27296.20		J 3→4 v = 0	
$v = 1, \ell = {}^+_- 1$	27297.18		F 4→4	36390.89
(ν_5)	27312.47		F 4→5	
$v = 1, \ell = {}^+_- 1$	27339.13		F 3→4	36392.36
(ν_6)	27360.47		F 2→3	
$v = 1, \ell = {}^+_- 1$			F 3→3	36394.18
(ν_7)			$v = 1, \ell = {}^+_- 1$	36395.91
F 3→3	27360.47		(ν_5)	36416.51
F 2→3	27361.12		$v = 1, \ell = {}^+_- 1$	36452.08
F 1→2	27361.51		(ν_6)	36480.69
F 3→4				

J = 3 →4 (Contd.)

Transition			Transition	
$v = 1, \ell = {}^+_- 1$			J 7→8 v = 0	72783.79
(ν_7)			$v = 1, \ell = {}^+_- 1$	72790.50
F 4→4			(ν_5)	72831.45
F 3→4	36481.72		$v = 1, \ell = {}^+_- 1$	72902.44
F 4→5			(ν_6)	72960.43
F 2→3	36481.88		$v = 1, \ell = {}^+_- 1$	72962.63
F 3→3	36483.28		(ν_7)	73067.27

Cyanoacetylene (Continued)

$J = 3 \rightarrow 4$ (Contd.) $v=1 \quad \ell = -1 \; (\nu_7)$		$J \; 9 \rightarrow 10 \quad v = 0$	90979.05
F $4 \rightarrow 4$	36532.94	$v = 1, \ell = \pm 1$	$\{$ 90987.30
F $3 \rightarrow 4$	36534.04	(ν_5)	$\{$ 91038.60
F $4 \rightarrow 5$ $\}$	36534.17	$v = 1, \ell = \pm 1$	$\{$ 91128.49
F $2 \rightarrow 3$ $\}$		(ν_6)	$\{$ 91200.03
F $3 \rightarrow 3$	36535.54	$v = 1, \ell = \pm 1$	$\{$ 91202.64
	36582.17	(ν_7)	$\{$ 91332.15
	36583.69	DCCCN	
$v = 2, \ell = 0 \pm 2$ $\{$ 36622.25		$J \; 3 \rightarrow 4 \quad v = 0$	33772.56
(ν_7) $\{$ 36623.51		$v = 1, \ell = \pm 1$	$\{$ 33796.03
		(ν_5)	$\{$ 33817.54
$v = 3, \ell = \pm 1$ $\{$ 36684.90		$v = 1, \ell = \pm 1$	33822.62
(ν_7) $\{$ 36789.99		(ν_6)	$\{$ 33847.40
$v = 3, \ell = \pm 3$ $\{$ 36737.14		$v = 1, \ell = \pm 1$	33852.65
(ν_7) $\{$ 36738.32		(ν_7)	$\{$ 33898.97
		$v = 2, \ell = 0 \pm 2$	33979.29
		(ν_7)	

The estimated experimental uncertainties are $\pm$ 0.1 Mc/s, except for lines of rare isotopic species, where the errors may reach twice this. Table 2 gives the derived rotational constants for the ground states, while the centrifugal distortion constants, D_J, are listed in Table 3, with values of the constants α, representing the effects of various vibrational quanta on the rotational constant B, and the corresponding ℓ-type doubling constants, q. For the assignments given, the line-frequencies calculated from these constants agree with observation within the error of measurement in virtually all cases. Relative intensities were in agreement with the assignments.

Stark effect displacements are summarised in table 4 for the $J = 0 \rightarrow 1$ transition of FCN and the $J = 0 \rightarrow 1$ and $1 \rightarrow 2$ transitions of FCCH. The effect of the small nuclear quadrupole splitting in FCN was neglected in comparison with the large Stark displacements.

TABLE 2

GROUND STATE ROTATIONAL CONSTANTS, B_o, (Mc/s)

Molecule	B_o (Mc/s)
FCN	$10,554.20 \pm 0.02$
$F^{13}CN$	$10,547.30 \pm 0.05$
$FC^{15}N$	$10,186.42 \pm 0.05$
$^{35}ClC^{15}N$	$5,743.061 \pm 0.03$
$^{37}ClC^{15}N$	$5,626.425 \pm 0.03$
FCCH	$9,706.19 \pm 0.01$
$F^{13}CCH$	$9,700.65 \pm 0.02$
$FC^{13}CH$	$9,373.94 \pm 0.02$
FCCD	$8,736.04 \pm 0.01$
$F^{13}CCD$	$8,733.92 \pm 0.02$
$FC^{13}CD$	$8,486.26 \pm 0.02$
$IC^{15}N$	$3,092.661 \pm 0.02$
$^{35}Cl^{13}CCH$	$5,655.57 \pm 0.03$
$^{35}ClC^{13}CH$	$5,469.73 \pm 0.03$
HCCCN	$4,549.06 \pm 0.01$
DCCCN	$4,221.58 \pm 0.01$

TABLE 3

ROTATION - VIBRATION CONSTANTS

		α Mc/s	q Mc/s	D_J Kc/s
FCN	ν_2	-30.39 ± 0.1	19.35 ± 0.1	5.3 ± 0.5
FCCH	ν_4	-27.65 ± 0.05	19.12 ± 0.05	3.6 ± 0.5
	ν_5	-8.92 ± 0.05	12.57 ± 0.05	
FCCD	ν_4	-24.56 ± 0.05	15.33 ± 0.05	2.6 ± 0.5
	ν_5	-15.15 ± 0.05	13.26 ± 0.05	
HCCCN	ν_5	-1.73 ± 0.02	2.56 ± 0.02	0.56 ± 0.01
	ν_6	-9.24 ± 0.02	3.57 ± 0.02	
	ν_7	-14.46 ± 0.02	6.54 ± 0.02	
DCCCN	ν_5	-4.28 ± 0.05	2.63 ± 0.05	
	ν_6	-7.81 ± 0.05	3.10 ± 0.05	
	ν_7	-12.91 ± 0.05	5.79 ± 0.05	

TABLE 4

STARK EFFECT MEASUREMENTS

FCN J 0 → 1

$E^2 \times 10^{-4}$ (v/cm)^2	30.90	85.84	123.60
$\Delta\nu$ Mc/s M = 0	9.21	26.34 v	37.54

$\mu = 2.17 \overset{+}{-} 0.05$ Debye units

FCCH J 1 → 2

$E^2 \times 10^{-4}$ (v/cm)^2	50.09	78.27	153.40
$\Delta\nu$ Mc/s M = 0	-0.48	-0.74	-1.56
M = 1	0.46	0.68	1.29

$\mu = 0.73 \overset{+}{-} 0.03$ Debye units

TABLE 5

MOLECULAR PROPERTIES

(All bond lengths in A)

	$\mu(D)$	Nuclear quadrupole coupling constant of nitrogen-14 (Mc/s)
H $\underline{1.063}$ C $\underline{1.155}$ N	3.00	$-4.58 \overset{+}{-} 0.05$
F $\underline{1.262}$ C $\underline{1.159}$ N	2.17	$-2.67 \overset{+}{-} 0.05$
Cl $\underline{1.631}$ C $\underline{1.159}$ N	2.80	$-3.63 \overset{+}{-} 0.1$
Br $\underline{1.789}$ C $\underline{1.158}$ N	· 2.94	$-3.83 \overset{+}{-} 0.08$
I $\underline{1.994}$ C $\underline{1.159}$ N	3.71	$-3.80 \overset{+}{-} 0.1$
F $\underline{1.279}$ C $\underline{1.198}$ C $\underline{1.053}$ H	0.73	-
Cl $\underline{1.637}$ C $\underline{1.204}$ C $\underline{1.055}$ H	0.44	-
H $\underline{1.058}$ C $\underline{1.205}$ C $\underline{1.378}$ C $\underline{1.159}$ N	3.6	$-4.28 \overset{+}{-} 0.05$

The Stark effects for these linear molecules are of the expected second-order type, and yield values of 2.17 $\overset{+}{-}$ 0.05 D and 0.73 $\overset{+}{-}$ 0.03 D for the electric dipole moments of FCN and FCCH respectively. The disagreement with the value earlier reported[1] for FCN arises from an error in calibration in the preliminary work. No measurements of dipole moment by dielectric methods are available for these substances.

Deutero-fluoroacetylene, FCCD, is an unusual example of a molecule in which deuterium is the only quadrupolar nucleus, and which has its $J = 0 \rightarrow 1$ transition in the 1 cm wavelength region. In view of the resolution[14] of deuterium quadrupole splitting in ClCCD an attempt was made to resolve such hyperfine structure in the $J = 0 \rightarrow 1$ line of FCCD at low gas-pressures in the video spectrometer. No splitting could be detected at a line-width of 150 kc/s at half intensity, and it was concluded that the deuterium coupling is not markedly greater than in ClCCD, where the splittings would be close to the resolution limit of our instruments.

In table 5 are listed the internuclear distances (r_s) determined by the isotopic substitution method from well known formulae summarized by Kraitchman[15]. With the data now reported, and existing measurements[16], all atoms have now been located in this way, except fluorine and iodine, where isotopic replacement is not normally possible. These atoms have been located from knowledge of the coordinates of all other atoms and of the centre of gravity of the molecule, in the way recommended by Costain[3], making use of the observation that the relation $\sum m x_s = 0$ is obeyed, where x_s is the substituion distance of an atom from the molecular mass centre. Since the truth of this relation is further confirmed here for chlorine cyanide and chloroacetylene, in which all atoms are located by substitution, the belief that F and I atoms are accurately located by this means in the related compounds is strongly supported. Also included in table 5 are the r_s- structure of bromine cyanide, entirely determinable from previous work[16], and the structure of hydrogen cyanide[3], as well as data on dipole moments and quadrupole coupling constants of nitrogen. The r_s- structure of cyanoacetylene[3], determined from the data of Westenberg and Wilson[17], is also included for comparison. Measurements on carbon-13 and nitrogen-15 species of HCCN and DCCN were also made during the present work; agreement with the findings of Westenberg and Wilson was very close, and our measurements give the same r_s- structure. In some instances, r_s- distances in these molecules can be computed independently in more than one way. In all such cases the

agreement between values is very close, within 0.001 A; a mean was taken in rounding the result to the nearest 0.001 A.

The accuracy of the internuclear distances is at present difficult to estimate absolutely. Costain[3] has expressed the view that r_s- distances, obtained from displacements similar to most of those concerned here, should be within 0.002 A of the equilibrium nuclear separations. Although such a view may be sometimes optimistic, we have adopted it for a general basis of discussion of our results, partly because it is a possible degree of accuracy, and one superior to that of other methods of estimating these distances at the present time, and partly because any deficiencies in the r_s- method should be less important when comparisons are made, as here, between series of molecules of closely related geometry. In fluorine cyanide and fluoroacetylene the carbon of the CF bond is within 0.1 - 0.18 A of the molecular mass centre, and the corresponding carbon-13 shifts, although accurately measured and still in the range estimated to be acceptable[3], are small. Hence it is these carbon atoms which, if any, might be somewhat less accurately placed than in the general case. Against this, it must be recorded that, when the location of the carbon of the CF bond is made independently in HCCF and CCCF, the r_s- distances are in very close agreement.

For fluoroacetylene, sufficient forms were studied for a check to be made[2] by means of the "double substitution" or "second difference" method described by Pierce[4]. In this, the r_s- coordinate (r_x) of an atom X is obtained for the original molecule, and again $(r_{x'})$ for a species substituted with extra mass Δ m at another atom, Y. The distance (r_y) of Y from the centre of gravity of the original species is then given by $(r_k - r_{k'})(M + \Delta m)/\Delta m$, M being the original molecular mass. If K is well away from the mass centre, $r_k - r_{k'}$ is accurately obtainable, and r_y may be computed. When data for FCCH, FCCD, $F^{13}CCH$ and $F^{13}CCD$ are used in this way to locate the carbon atom of the CF bond, its r_y is found as 0.1744 A, as against 0.1740 A from the direct isotopic shift. This agreement thus lends support to the distances found in the simpler way. If the "double substitution" coordinate is used for this

atom in conjunction with r_s coordinates for the remainder, fluorine being located as already indicated, the structure becomes $CF = 1.280$ A, $CC = 1.197$ A, $CH = 1.053$ A, hardly differing from that in table 5.

Enough data are available to apply the second difference method to locate all isotopically replaceable atoms in fluoroacetylene. The present data, so applied, give the structure: $CF = 1.284$ A, $CC = 1.203$ A, $CH = 1.058$ A. There is, however, no proven disagreement with the tabulated r_s structure, since it should be emphasized that the second difference method makes exceptional demands on the accuracy of the rotational constants, or at least of their isotopic shifts. This is apparent from the relationship mentioned, through which uncertainties in r_k are multiplied in r_y by the ratio $(M + \ldots m)/\Delta m$, here about 45. Even with the very small uncertainties in B_0 values given in table 2 for fluoroacetylene, it still emerges that coordinates of all atoms located by second differences are uncertain by some ± 0.005 A from possible errors in relative B_0 values alone. Hence the usual r_s - structure is much to be preferred at present; the improbability of the structure derived above entirely by the double substitution method may be emphasised by noting that it would have a moment of inertia nearly 1% greater than the observed ground state moment. As high frequency studies permit continued refinement of rotational constants for the necessary isotopic forms, closer comparison of structures from the single and the double substitution methods will be possible.

DISCUSSION

The CF distances measured here are the first to be determined for carbon atoms triply bonded to a second ligand; they are easily the shortest CF distances yet found, that in fluoracetylene being some 8% shorter than the 1.38 A found in methyl fluoride[18] and ethyl fluoride[19], while the CF in fluorine cyanide is 9% shorter than the same value. In vinyl fluoride[20] and other substances containing the group $=CHF$[21], the CF length (1.34A - 1.35A) is some 3% less than in alkyl fluorides. These percentage

shortenings are close to those found for CCl bonds in the series: ethyl chloride[22] (1.788A), vinyl chloride[23] (1.726A) and chloracetylene (1.637A) or chlorine cyanide (1.631A). The CCl in chloracetylene is some 0.005A longer than the length previously reported[24] from more restricted microwave data which did not allow r_s-distances to be computed. The new length agrees closely with that in methyl chloracetylene[25], as predicted by Costain[25] on the basis of the equality of the chlorine quadrupole couplings in these two substances.

A discussion of the nature of the carbon-halogen bonds in these substances, based purely on their lengths, can be given in various terms, but is inconclusive regarding the question of how much double-bond character is involved. Shortenings expected on account of reduction of the carbon bond-radius with increasing s-character in carbon bonding orbitals[26] are less than those observed, provided constant halogen radii are assumed. Thus the maximum shortenings due to changes in carbon radius which might reasonably occur are the changes in "single" carbon-carbon bond lengths in propane[27] (1.526A), propene[28] (1.501A) and methyl acetylene[29] (1.458A), and even part of these shortenings can legitimately be regarded[30] as due to hyperconjugation. A more complicated situation is thus very probable for the carbon-halogen bonds in these substances. Explanations which do not necessarily involve double-bond character might ascribe important effects to the presence or absence of interactions between non-bonded atoms[31], or to variations in hybrid zation of orbitals in accordance with electronegativities of substituents,[32] but quantitative discussion is difficult. On the other hand, a model which allows conjugation effects to confer some double-bond character on the shorter carbon-halogen bonds[23,33,34] permits the simplest explanation of the results, and conforms with a reasonable and widely held view. Pauling[35] has emphasized that such double-bond character would be especially favoured when, as in the present linear molecules, two equivalent pairs of π-orbitals can be used by the atoms concerned. Accordingly we regard the CF bonds in fluorine

cyanide and fluoroacetylene as possessing double bond character, although quantitative estimates are prevented by the difficulties in ascribing atomic radii. A tendency of fluorine, as a first-row element, to form double bonds accords with general chemical experience, but in the molecules under discussion the effects for fluorine are no greater than those for chlorine. It is notable, however, that the CF distance in FCN is 0.017A shorter than in fluoroacetylene, while in the analogous chlorine compounds the difference, though in the same direction, is only 0.006A.

The stretching force constant for the CF bond in FCN was determined by Dodd and Little[36], and that for CF in fluoroacetylene by Brown and Tyler[37]. Similar treatments for fluoroacetylene and other halogenated acetylenes were given by Hunt and Wilson[38]. These carbon-halogen force constants are all much higher than in corresponding alkyl halides and are to be correlated with them through concepts similar to those mentioned in discussing the bond-lengths.

The nature of the CX bonding in the XCN series should be reflected in properties of the CN linkage and in the nuclear quadrupole coupling of the nitrogen-14 atom. In FCN this coupling is the smallest yet found for a cyanide group, being only some 58% of than in HCN. The nitrogen couplings decrease as we move along the XCN series in the order X = H, I, Br, Cl, F (Table 5). This is in agreement with the suggestion of Townes and Dailey, and others[39], that states containing $C = N^-$, with low quadrupole coupling, increase in importance in the same X sequence. In early work[40], this sequence was also believed to be accompanied by a small steady increase in CN length, but the present results show that the substitution CN distance is very close to 1.159A in all the halogen cyanides, though this is probably slightly longer than the value in HCN. Thus, while CN lengths suggest that states containing $C = N^-$ are somewhat more important in the halogen cyanides than in HCN, they give no indication of a variation within the halogen cyanides themselves.

It has been stressed, however,[30], that the effect of states such as those containing $C = N^-$ on the lengths of what are formally triple bonds would be very small, and could be masked by other influences.

In particular, the CN distances show no change parallelling the large diminution in quadrupole coupling of the nitrogen in passing from ClCN to FCN. Hence the CN bonds in the halogen cyanides, while possessing the same substitution internuclear distances, have demonstrably different electronic distributions, as indicated by the quadrupole couplings. This is as clear a demonstration as present methods allow that bonds of equal length are not necessarily equal in their other properties.

The CN-stretching force constants in the XCN series[38] are all very similar, and can probably not at present be used with sufficient precision to check deductions made from the other data.

Probably the best general description of the structures of the halogen cyanides is one based on the views of Casabella and Bray[41], who used also the evidence of the halogen quadrupole coupling data. Three main states are regarded as present, $X - C \equiv N$, $X^+ = C = N^-$ and $X^- \quad C^+ \equiv N$, of which the last two are both believed to increase in importance in the sequence X = I, Br, Cl, F. From figures given by Casabella and Bray, it would be reasonable to suppose that FCN contains contributions of some 10-20% of both these last two forms. The contribution of the second state accounts qualitatively for the dependence of nitrogen coupling on the nature of X, while the constancy of the CN distance might arise from parallel changes in contributions of $X^+ = C - N^-$ and $X^- \quad C^+ \equiv N$, the first of which favours lengthening of the CN bond, and the second its shortening through the effect of the positive charge on the carbon radius. The experimental data at present do not justify postulation of forms containing $C = N^+$ as suggested by Dodd and Little[36]; having incomplete octets, these would be of little importance.

When CC bonds are compared similarly in the XCCH series, a slightly different situation is found. The CC bond in ClCCH has a substitution length equal to the 1.204Å found in acetylene itself[42], rather than the 1.211Å reported earlier[24]. Accordingly, a lengthening such as occurs in the CN bond on passing from HCN to ClCN does not appear in comparing CC bonds in HCCH and ClCCH, while in FCCH the CC bond is probably shorter than that in acetylene by some 0.006Å. This parallels a shortening of the $C=C$ bond in olefins[43] as they are increasingly substituted by fluorine. The effects are possibly due in part to an increasing contribution of $X^{-}-C^{+}\equiv CH$ along the sequence X = H, Cl, F, a shrinkage of CC due to this form being here not cancelled entirely by accompanying contributions of forms such as $X^{+}=C-\overline{C}H$, though these probably occur. The effects are small, however, and, as Duchesne has emphasised[44], other factors such as hybridization could be significant. The CC-stretching force constants[38] are here also very similar in all the XCCH series, and cannot at present be used to decide among alternative interpretations.

The electric dipole moments of the XCN and XCCH series (Table 5) conform in general with interpretations of structure indicated above. The moments of FCN and FCCH fit well with expectations from the trends in moments of the other members of the series, that for FCN being the smallest and that for FCCH the largest in their respective families. Beyond reasonable doubt, the negative poles of the dipoles are directed towards nitrogen in XCN and towards X in XCCH. The strikingly small moments of FCCH and ClCCH, coupled with the zero moment of BrCCH[45], suggest strongly effects similar to those already favoured by other evidence, although again the relative importance of different effects on the dipole moment cannot be absolutely decided.

In the course of this work we made[37] the first authentic specimens of iodoacetylene and iodoacetylene-d, and characterized them by mass-

and infra-red spectra. Careful attempts, using intense Stark fields, have
so far failed to detect a microwave spectrum of iodoacetylene, which
strongly suggests that its dipole moment, like that of BrCCH, is less
than some 0.01D. Stark modulation of the ground state spectrum would
then require very large fields indeed in such a molecule, but the l-
type doublet spectra of the reasonably well populated vibrational states
should be more easily modulated, and have not been detected.

The centrifugal distortion and vibration-rotation interaction constants
in Table 3 are worth brief comment. The newly determined distortion
constants D_J have the orders of magnitude expected from considerations
of atomic masses and force fields involved. Thus D_J for cyano-
acetylene is about the same as those found for diacetylene[46] and
cyanogen[47]. Calculations of D_J for FCN from vibrational data[48] at
present yield a value somewhat lower than that tabulated, although more
recent measurements in the millimetre wavelength range made in this
laboratory[49] give a refined value of D_J for FCN as 4.91 ± 0.02 kc/s,
and confirm the tabulated constant for HCCCN to higher accuracy.

The constants a and q in Table 3 follow patterns consistent with
expectations from data in related molecules. The values of q accord
approximately with the rule $q = \underline{a}B_0^2 / \omega$ (ω = vibration frequency), the
factor $\underline{a}$ having values between 2 and 2.6. On the assumption that
$\underline{a}$ retains its same value for a given vibration, we may use the constants
q for cyanoacetylene and the known values ν_5, ν_6 and ν_7 for
HCCCN to estimate the frequencies for DCCCN as 546 cm^{-1}, 498 cm^{-1}
and 224 cm^{-1}, as compared with 663 cm^{-1}, 502 cm^{-1} and 230 cm^{-1} for
HCCCN[50].

In the $J = 3 \to 4$ transition of HCCCN spectra due to molecules in
the $v = 1$, $v = 2$ and $v = 3$ levels of the lowest mode (ν_7) were measured.
The coupling constant of nitrogen in the $v = 1$ state was virtually the
same as in the ground state. The fine structure of the $v = l = 2$ and
$v = l = 3$ lines (Table 1) is noticeable, and the presence of intense

spectra for molecules in such levels in cyanoacetylene may justify
a closer study later.

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STRUCTURAL STUDIES OF LINEAR MOLECULES
BY MICROWAVE SPECTROSCOPY

J.K.Tyler and J.Sheridan　　Mar. 1963

ABSTRACT: Detailed studies of molecular geometry
by isotopic substitution in FCN, ClCN, ICN, FCCH
and ClCCH. Also spectroscopic data for HCCCN.

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